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This technical memorandum (TM) is designed to provide revised estimates for the mass of chlorobenzene (MCB) within the Upper Bellflower Aquitard (UBA) beneath the Montrose facility, and to provide the basis for those revised estimates. Estimates have been made for (1) the existing condition, (2) the predicted condition after completion of a hydraulic displacement (HD) remediation, and (3) the predicted condition after completion of steam remediation, assuming steam remediation can reduce DNAPL saturations to between 0.5 percent and 4 percent.

Approach

Without a high vertical density of soil sampling, if is difficult to provide an accurate estimate of DNAPL mass in the subsurface. Instead a variety of approaches can be used, and have been used to estimate DNAPL and MCB mass at Montrose over the years. These approaches have most commonly combined the thickness of observed DNAPL with peak DNAPL or MCB concentrations measured in the soil. A common criticism of those estimates by EPA has been that the measured soil concentrations of DNAPL are inconsistent with the assumed or observed thickness of DNAPL from the boreholes. For example, soil concentrations of MCB of more than 50,000 mg/kg have been associated with reported soil thicknesses of several tenths of a foot, whereas capillary theory requires several feet of DNAPL to create enough capillary pressure to produce the observed soil saturations (concentrations). In previous documents by Montrose, both "conservative" and "liberal" estimates of DNAPL mass have been provided. In the FS, Montrose has chosen to conduct its analysis based upon only the "liberal" mass estimate. In this most recent effort, it appears that Hargis & Associates has made an attempt to take into account the thickness of DNAPL necessary to create the capillary pressures required to account for the observed soil concentrations. Using the observations in borehole PSB-4, for example, a maximum DNAPL concentration of 82,000 mg/kg (45,000 mg/kg MCB concentration) was observed in the interval from 88 to 88.1 ft bgs, with minor concentrations observed over an additional 0.3 ft of the borehole. In the previous "conservative" estimates, the mass of MCB would be estimated by multiplying the 45,000 mg/kg concentration by the total 0.4 ft of observed occurrence of DNAPL in the borehole. The "liberal" estimate uses a thickness of 2.9 ft (presumably calculated as the minimum thickness of DNAPL to produce a maximum MCB concentration of 45,000 mg/kg) and multiplies it by the peak saturation of 45,000 mg/kg to arrive at an estimate of mass (Figure 1).

The alternate approach described in this TM is to calculate the profile of DNAPL saturation vs. depth, converted to MCB concentration vs. depth, that results in the peak measured concentration of MCB at the base of the impacted interval (Figure 1). The basis of this calculation is the relation between NAPL saturation and capillary pressure given by the Van Genuchten equation:

$$S_w = (1 - S_{wr}) \bullet \left[\frac{1}{1 + \left(\alpha_{ow} h_c^{ow} \right)^n} \right]^{\left(1 - \frac{1}{n}\right)} + S_{wr} \qquad (1)$$

and $S_o = 1 - S_w$ (2)

where S_o is the oil (NAPL) saturation, S_w is the water saturation, S_{wr} is the residual saturation of the water phase, h_c^{ow} is the capillary pressure head of the oil-water phases, α_{ow} is the oil-water Van Genuchten soil parameter related to soil entry pressure, and n is the Van Genuchten soil parameter related to the slope of the relation between capillary pressure and fluid saturation. The value of α_{ow} can either be measured directly by displacing water with the DNAPL of interest, or can by calculated by scaling it from a measured value of α_{aw} using

$$\alpha_{ow} = \alpha_{aw} \bullet (\sigma_{aw} / \sigma_{ow}) \qquad (3)$$

where α_{aw} is the Van Genuchten capillary parameter for an air-water system and $\sigma_{aw,ow}$ are the air-water and oil-water interfacial tensions, respectively.

The relation between the capillary pressure head (h_c^{ow}) and the depth below the water-DNAPL interface (d) under vertical equilibrium conditions is given by:

$$h_c^{ow} = (\rho_r - 1) \bullet d \qquad (4)$$

where ρ_r is the relative density of the DNAPL.

Because the focus of the mass estimates at the Montrose facility is the mass of MCB, the DNAPL saturations calculated with equations (1) to (4) above were converted to mass of MCB, using:

$$M_{MCB} = \frac{S_o f_{MCB}\, n\, \rho_o \bullet (1000\, mg / gm)}{\left[\frac{(1-n)\rho_g}{1000\, gm / kg} \right]} \qquad (5)$$

where MCB is the mass of MCB (in mg of MCB per kg of soil), MCB is the fraction of the DNAPL that is MCB, n is the porosity of the soil,   is the density of the DNAPL (in gm/cc), and is the soil grain density (in gm/cc).

The above equations (1) through (5) were applied for depths below the DNAPL/water interface of 1 cm to 137 cm (0.1 ft to 4.5 ft) assuming a DNAPL density of 1.247 gm/cc, an MCB fraction of 50%, a NAPL/water interfacial tension of 23.6 dynes/cm, in a soil that has an air/water Van Genuchten (VG) capillary parameter alpha of 0.01/cm a VG n of 2.62, a residual saturation for the water phase of 0.045, a porosity of 0.42, a soil grain density of 2.65 gm/cc. Using borehole PSB-4 as an example an equilibrium distribution of DNAPL would require an accumulated thickness of 3.9 ft of DNAPL, and MCB concentrations would vary from zero at the DNAPL/water interface to 45,000 mg/kg at the base of the DNAPL accumulation (Figure 1).

The total mass is the integral of the mass/depth profile. This approach results in a smaller estimate of MCB mass (2500 gm/sq ft) than that calculated in the FS (6000 gm/sq ft).

The complete calculations of DNAPL saturations and corresponding DNAPL mass concentrations, MCB mass concentrations, and the integral of DNAPL and MCB mass from the DNAPL/water interface downward under non-remediated conditions are provided in the worksheet "DNAPL Distribution Table" within the "Huntley Modified Mass Estimates.xls" Excel Workbook, included with this TM. The calculated DNAPL saturations (as a function of depth below the DNAPL/water interface) are in column E, DNAPL soil concentrations (in mg/kg) and vertical (downward) integral are found in columns F and G, respectively, and the corresponding MCB soil concentrations and vertical integral are found in columns H and I, respectively.

Calculation of the mass of DNAPL and MCB after remediation is based on the above calculated profiles and the saturation (or concentration) left behind after remediation. For example, laboratory testing of soils of the UBA suggest that ambient-temperature displacement of the Montrose site DNAPL by water (the HD remediation) will leave behind a DNAPL saturation of 19 percent, corresponding to an MCB concentration of about 32,000 mg/kg. Estimation of the mass remaining in the soil after HD remediation, then, is a simple matter of modifying the predicted MCB concentration profile (column H of the attached worksheet "DNAPL Distribution Table") by reducing the concentrations to 32,000 mg/kg for those depths where the initial concentration was above 32,000 mg/kg, and keeping unchanged those concentrations that were initially at or below 32,000 mg/kg (see Figure 1 below and column J of excel worksheet) and calculating the new integral mass of MCB as a function of thickness of DNAPL (column L). The same approach was applied to steam remediation, for a range of estimated post-remediation saturations of 0.5 percent (1,704 mg/kg MCB) to 4 percent (13,600 mg/kg) and is shown conceptually for borehole PSB-4 in Figure 1. The resulting predicted concentration profiles are provided in columns P and M, respectively of the attached worksheet ("DNAPL Distribution Table") and the vertical integral mass estimates for varying thicknesses of DNAPL are provided in columns R and O of the worksheet, respectively.

The relations between the mass of MCB and the thickness of accumulated DNAPL derived above could be applied to the Montrose site if the distribution of accumulated thickness of DNAPL as a function of x,y,z space were well-known. However, the database for Montrose consists of select measured soil concentrations and observed thicknesses, many of which are inconsistent with the soil concentrations. To account for the uncertainty in the thickness, Montrose calculated the necessary thickness to account for the peak measured MCB concentration, then multiplied that peak concentration by the calculated thickness to obtain a mass estimate for that borehole. To integrate that estimate aerially, Montrose measured the area where peak DNAPL concentrations exceeded 50,000 mg/kg, were between 10,000 mg/kg and 50,000 mg/kg, were between 1,000 mg/kg and 10,000 mg/kg, and were less than 1,000 mg/kg and multiplied the average MCB (or DNAPL) mass within each area by the measured areas to obtain (after summing) the total mass.

The alternate approach described in this TM assumes that the peak concentration measured in each borehole is the maximum concentration within the profile and calculates the integral mass of the resulting profile. To apply this to the measurements of peak concentration provided by Montrose, a relation between the peak concentration of MCB and the integral mass of MCB in the profile is needed. This could be obtained manually by simply comparing columns H and I (in worksheet "DNAPL Distribution Table"), but that manual approach is somewhat tedious when applied to more than 80 boreholes, and does not take advantage of the spreadsheet environment. To allow automated calculation of the mass of MCB as a function of peak measured MCB concentrations, first under unremediated conditions and later for HD and steam remediation, polynomial regression equations were fit to the exact, calculated relations between peak MCB concentrations and vertically-integrated MCB mass. In all cases, a 2nd order polynomial of the form $M_{MCB} = AC^2_{MCB} + BC_{MCB} + I$, where M_{MCB} is the vertically integrated mass of MCB for a borehole location (in gm/sq ft), C_{MCBA} is the peak concentration of MCB (in mg/kg), and A, B, and I are the polynomial regression coefficients. Table 1 summarizes the resulting regression coefficients for initial (unremediated) conditions and for each of the analyzed remediation approaches, and Figure 2 shows the fit between the polynomial regression equations and the exact relations calculated with equations (1) through (5).

Table 1. Regression Coefficients Derived for Relation Between Peak MCB Concentrations and Vertically-Integrated Mass of MCB.

Condition	Regression Coefficients			Multiple Correlation Coefficient
	A	B	Intercept I	
Initial (no remediation)	9.07E-07	0.013	0.35	0.999
HD	5.29E-07	0.026	-38.8	0.999
Steam-1	-1.11E-08	0.031	-36.5	0.999
Steam-2	-4.66E-08	0.007	9.95	0.996

Results

The above regression relations were used to modify the worksheet provided by Montrose used for their estimate of MCB mass. Their worksheet provided, for each borehole, the boring ID, the peak MCB concentration, their calculated integral mass, and a classification scheme that placed each borehole, on the basis of the peak MCB concentration, in the area of greater than 50,000 mg/kg peak DNAPL concentration, 10,000 mg/kg to 50,000 mg/kg peak concentration, 1,000 mg/kg peak concentration, and less than 1,000 mg/kg peak MCB concentration. That provided worksheet was modified by re-calculating column I, the calculated integral mass using the regression equations described above and the peak MCB concentration given in column C of the provided worksheet. This was done separately for the initial conditions (worksheet “Initial” within workbook “Huntley Modified Mass Estimates.xls”), the HD remediation (worksheet “HD Remedy” within workbook “Huntley Modified Mass Estimates.xls”), steam remediation with an assumed reduction to no more than 4% DNAPL saturation (worksheet “Steam Remedy-1” within workbook “Huntley Modified Mass Estimates.xls”), and steam remediation with an assumed reduction to no more than 0.5% DNAPL saturation (worksheet “Steam-Remedy-2” within workbook “Huntley Modified Mass Estimates.xls”).

The results for the four cases are summarized in tables 2 through 5 (also included in the attached workbook).

Table 2. Calculated Total Mass of MCB Under Initial (Unremediated) Conditions

	Contour Area				
	>50,000 mg/kg	>10,000 mg/kg	>1,000 mg/kg	<1,000 mg/kg	
Average (gm/sq ft) =	3651.0583	328.4760	34.9893	4.0517	Subtotal
Area (sq ft) =	30,492	58,141	50,447	23,045	162,125
MCB Mass (lbs) =	244,922	42,015	3,883	205	291,026
% of Total Mass =	84.2%	14.4%	1.3%	0.1%	100.0%

Table 3. Calculated Total Mass of MCB After HD Remediation

	Contour Area				
	>50,000 mg/kg	>10,000 mg/kg	>1,000 mg/kg	<1,000 mg/kg	
Average (gm/sq ft) =	3000.6018	367.8312	26.3110	0.0000	Subtotal
Area (sq ft) =	30,492	58,141	50,447	23,045	162,125
MCB Mass (lbs) =	201,288	47,049	2,920	0	251,257
% of Total Mass =	80.1%	18.7%	1.2%	0.0%	100.0%

It should be noted that a comparison of estimated masses after HD remediation (Table 3) to that under initial conditions (Table 2) implies a reduction in mass in areas that have peak DNAPL concentrations of less than 50,000 mg/kg. This is an artifact of the use of a polynomial regression equation, instead of the exact relation between peak concentration and integral mass. Because these differences are small, however, no correction has been made.

Table 4. Calculated Total Mass of MCB After Steam Remediation Assuming Maximum Remaining DNAPL Saturation of 4 Percent

	Contour Area				
	>50,000 mg/kg	>10,000 mg/kg	>1,000 mg/kg	<1,000 mg/kg	
Average (gm/sq ft) =	1504.2582	334.7179	35.6767	0.0000	Subtotal
Area (sq ft) =	30,492	58,141	50,447	23,045	162,125
MCB Mass (lbs) =	100,909	42,814	3,960	0	147,683
% of Total Mass =	68.3%	29.0%	2.7%	0.0%	100.0%

Table 5. Calculated Total Mass of MCB After Steam Remediation Assuming Maximum Remaining DNAPL Saturation of 0.5 Percent

	Contour Area				
	>50,000 mg/kg	>10,000 mg/kg	>1,000 mg/kg	<1,000 mg/kg	
Average (gm/sq ft) =	217.7931	86.7036	24.0193	11.8571	Subtotal
Area (sq ft) =	30,492	58,141	50,447	23,045	162,125
MCB Mass (lbs) =	14,610	11,090	2,666	601	28,967
% of Total Mass =	50.4%	38.3%	9.2%	2.1%	100.0%

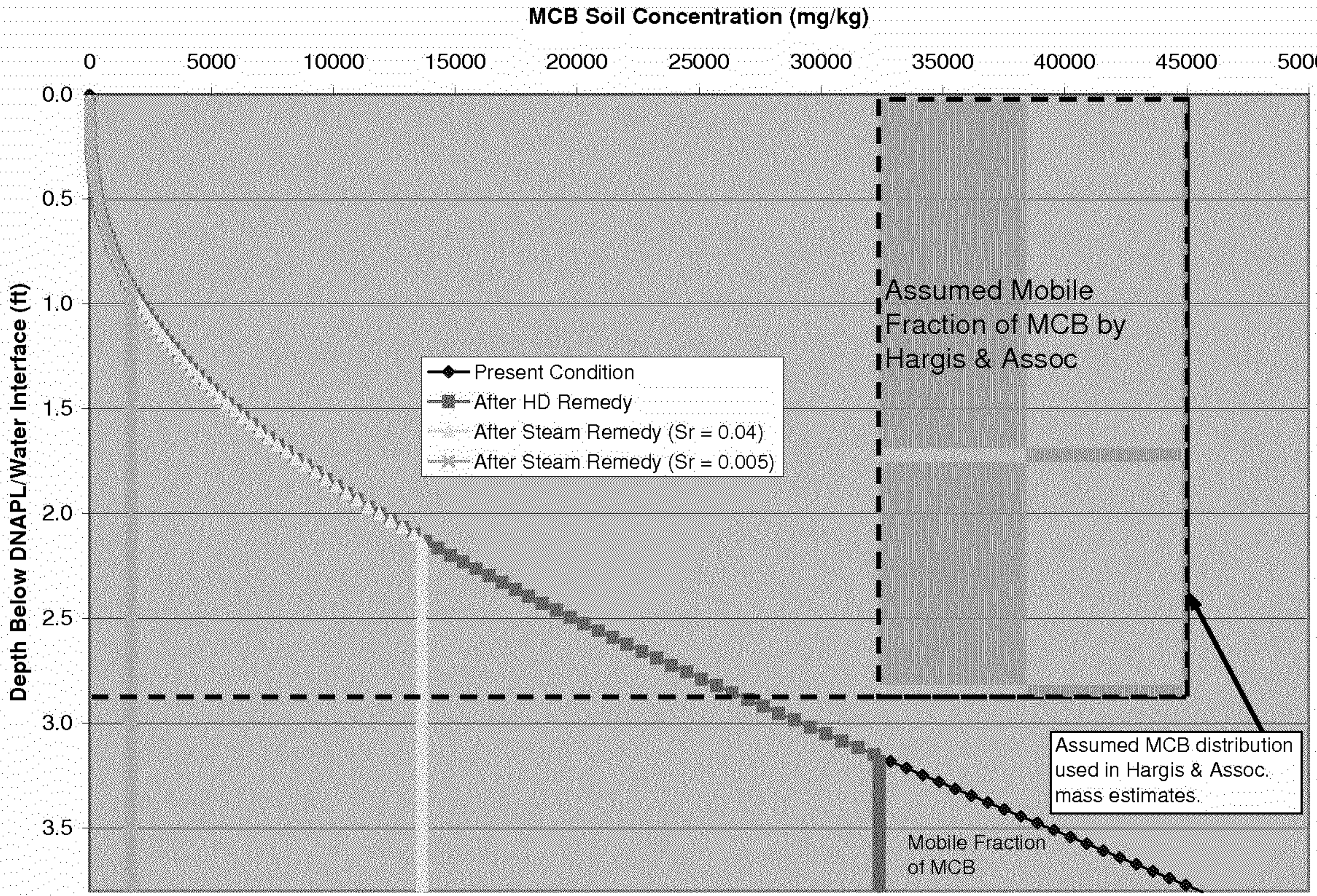

Figure 1. Example of MCB distribution in soils adjacent to borehole PSB-4, comparing profile consistent with capillary theory to profile assumed by Hargis Assoc. for Montrose FS.

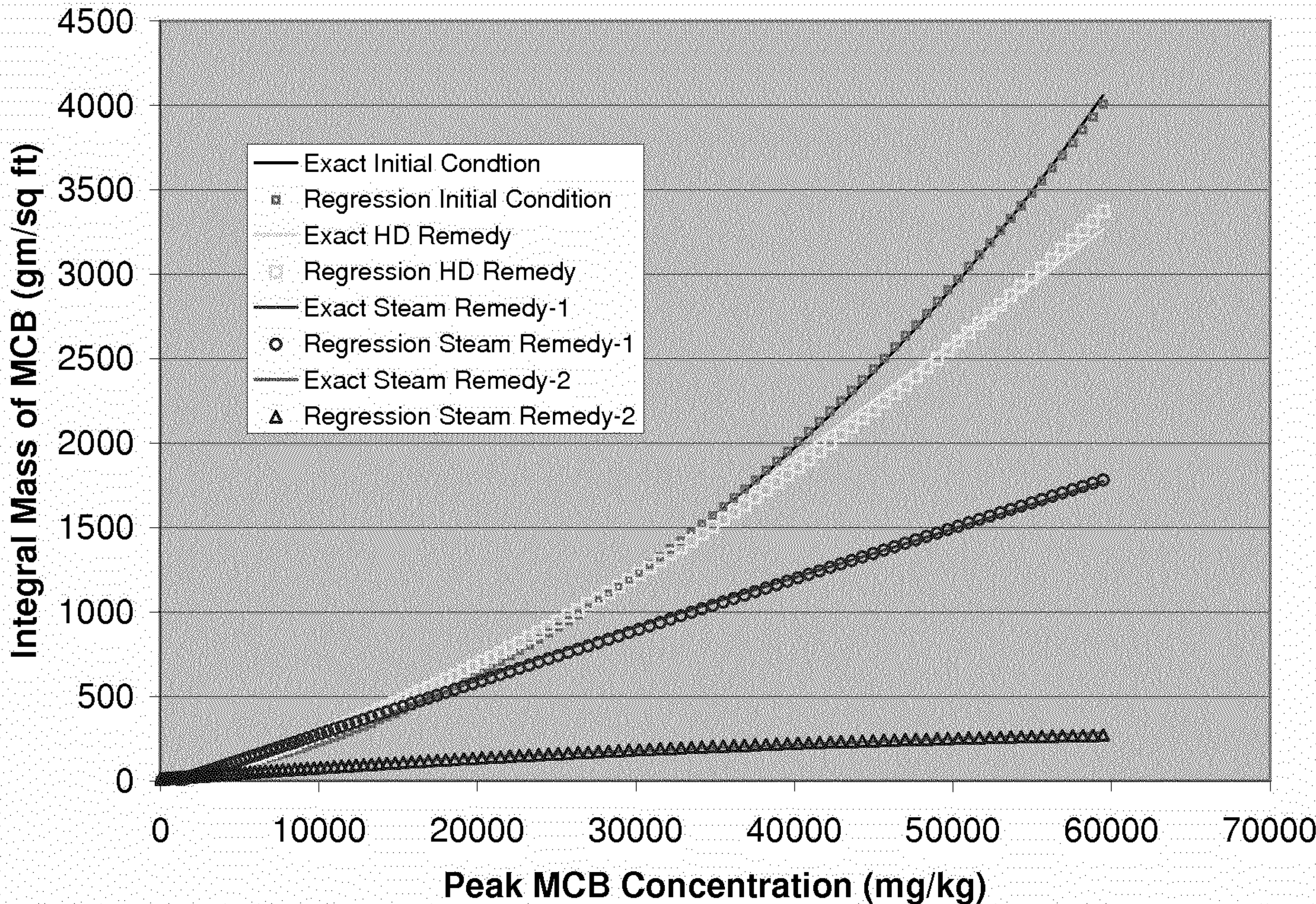

Figure 2. Comparison of exact relation between peak MCB concentration and vertically-integrated mass of MCB and approximate regression relations.